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(21) International Application Number: PCT/EP91/00577 (22) International Filing Date: 21 March 1991 (21.03.91) (30) Priority data: 9006549.1 23 March 1990 (23.03.90) GB (71) Applicant (for all designated States except US): EXXON CHEMICAL LIMITED [GB/GB]; Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB). (72) Inventor; and (75) Inventor/Applicant (for US only) : VANHAEREN, Gerald, Marie [BE/BE]; Rue Denis Deceuster 41B, B-1330 Rixensart (BE).		(74) Agents: BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, PO Box 1, Abingdon, Oxfordshire OX13 6BB (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CROSS-LINKABLE ADHESIVE COMPOSITION (57) Abstract A curable adhesive composition includes (a) a copolymer of at least 50 wt% ethylene and containing from 0.10 to 0.35 mole of hydroxyl functionality per 100 gm of polymer; (b) a compound containing isocyanurate groups and at least two terminally blocked isocyanate groups; (c) optionally a hydrocarbon tackifying resin, and optionally a low molecular weight hydroxy-terminated polyalkylene oxide containing at least three hydroxyl groups or other viscosity reducing agent.		

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CROSS-LINKABLE ADHESIVE COMPOSITION

Field of invention

This invention relates to cross-linkable compositions which may be applied as a film or as a melt and subsequently cured at a temperature above the application temperature.

Background of invention

Hot melt adhesives based on ethylene-vinyl acetate copolymers are known. Although effective for certain applications, they fail in certain assembly applications due to their poor cohesive properties at temperatures of above about 60°C. In these cases, the bond strength develops on cooling but the cohesive properties are always limited at a given temperature due to the thermoplastic nature of the hot melt components.

Compositions capable of providing high adhesion with good heat resistance are suggested in Japanese Patent Publication 58-217575 (Yunichika) which discloses a hot-melt adhesive comprising firstly a saponified ethylene/vinyl acetate copolymer, secondly a polyisocyanate having at least two masked isocyanate groups per molecule and thirdly, a terpene phenol resin and/or a liquid polybutadiene having at least two hydroxyl groups per molecule. The reactive copolymer may have a melt flow index as from 0.5 to 200. The saponified EVA has 10 mol % of vinyl alcohol units and has a melt index of 170 in the example 1. A wide variety of masking agents are disclosed.

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EP 30594 (Bayer) discloses a coating powder containing hydrolysed vinyl acetate copolymer and polyuretonimines obtained by reaction of polycarbodiimides and di- and tri-isocyanates.

GB 1079749 (ICI) describes a cross-linkable coating composition (for moulding into pipes and hoses and for cables and wires for example) not as such suitable for hot melt adhesive compositions containing a polymer of a monoethylenically unsaturated monomer and units having certain functional groups a.o. hydroxyl, and a polyisocyanate generator including aromatic internally blocked isocyanates such as specified uretidione aromatic dimers and alkylene uretidione dimers in general. The blocked products have a rate of decomposition varying with temperature which causes cross-linking at temperatures above 120°C.

EP-A-0041.192 (Siemens) describes the production of crosslinked polyolefin based cable and wire insulation and sheet production by crosslinking hydroxyl containing polyolefin with blocked polyisocyanate.

EP-A-0294.271 (Atochem) describes a crosslinkable adhesive composition based on ethylene vinyl acetate copolymer containing primary hydroxyl functionalities. The terpolymer is obtained by introducing, by grafting or direct copolymerization, an ethylenic monomer containing a primary hydroxyl such as 2-hydroxy ethyl acrylate or methacrylate. The copolymer contains from 0.02 to 0.15 moles of primary hydroxyl per 100 gms. The

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adhesive composition also contains a blocked polyisocyanate and a tackifying resin which may be used as blocking agent of the polyisocyanate. The preferred polyisocyanates are diisocyanates such as toluene diisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate or isophorone diisocyanate.

EP-A-0302.620 (Exxon) discloses the use of saponified EVA's having at least 5 % wt % of vinyl alcohol derived units (14.75 wt % and 10 wt % in Examples) cured with an internally blocked polyisocyanate in the presence of a viscosity reducing component. The saponified EVA may have a viscosity of from 1 to 100 Pa.s, preferably 4 to 40 Pa.s, at 180°C and have a preferred melt flow index of from 10 to 2500.

Japanese Patent publication 4640419 (Miura) relates to heat reactive, heat sensitive elastomer composition in which saponified EVA is crosslinked by an isocyanate adduct including lactam derivatives with a decomposition promoter. Example 1 uses an EVA with 11.2 wt % of vinyl alcohol derived units. Phenol adducts are used in the Examples which release volatile phenols in use.

It is amongst the aims of the invention to provide a hot melt adhesive composition curable by heating, which is stable before curing, which can be cured safely in a controllable manner at elevated temperatures appropriate to hot melt adhesive application, has a desired balance of properties for convenient application and provides a thermally stable bond.

Summary of invention

According to this invention there is provided a hot melt adhesive composition comprising :

- (a) a copolymer of at least 50 wt% ethylene and containing from 0.10 to 0.35 mole of hydroxyl functionality and having a melt viscosity of from 1 to 50 Pa.s at 180°C;
- (b) a compound containing isocyanurate groups and at least two terminally blocked isocyanate groups;
- (c) optionally a hydrocarbon tackifying resin, and optionally a low molecular weight hydroxy-terminated polyalkylene oxide containing at least three hydroxyl per mole.

Other ingredients such as carbon black, and fillers such as calcium carbonate and silicates can also be added to impart particular properties to the compound.

Suitably the copolymer (a) is a polymer having monomeric units of ethylene and of vinyl alcohol, and optionally vinyl acetate, the melt viscosity being from 1 to 50 Pa.s at 180°C, preferably from 3 to 40 Pa.s at 180°C. Ethylene vinyl alcohol copolymers contain at least 0.10 mole of hydroxyl functionality per 100 gm of copolymer (or 4.4 wt% vinyl alcohol), preferably at least 0.16 mole OH per 100 gm of copolymer (or 7.0 wt% vinyl alcohol units). One example is a terpolymer (viscosity 25 Pa.s at 180°C, MFR at 125°C under 325 gm

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load of 6.4 gm/10 min.) with 10 % vinyl alcohol (or 0.227 moles per 100 gms), 88.75 % ethylene and 1.2 wt% vinyl acetate. The m.p. is 101.5°C (by DSC). Another terpolymer contains 13.7 wt% vinyl alcohol (or 0.311 mole per 100 gms), 82.3 % ethylene and 4.0 wt% vinyl acetate (viscosity 5.8 Pa.s at 180°C, MFR at 125°C under 325 gm of 30.4 gm/10 min., DSC m.p. 91°C). Copolymers of the above stated type help to provide a suitable characteristic to the hot melt adhesive composition.

The copolymers including those referred to above, may be copolymers of ethylene and vinyl alcohol obtained by hydrolysis or transesterification of ethylene-vinyl carboxylate (e.g. ethylene-vinyl acetate) copolymer. The degree of hydrolysis can be partial or total, partial hydrolysis leaving some ester groups in the polymer.

Usually the carboxylic acid from which the carboxylate is derived has from 1 to 6 carbon atoms per molecule and the especially preferred vinyl carboxylate from which the vinyl alcohol is derived is vinyl acetate. The transesterification may be effected by reaction in the melt stage at about 100°C with, for example, n-butanol using sodium methyle as a catalyst.

The preferred copolymers of ethylene and vinyl alcohol are obtained from ethylene vinyl acetate copolymers having a melt flow index (ASTM D1238 52 T) of 250 to 3000, preferably from 400 to 2000, and comprise preferably at least 70 wt % of ethylene and at least 7 wt % of vinyl alcohol units.

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Suitably the copolymer (a) containing hydroxyl functionality may also be a copolymer of ethylene and 2-hydroxyethyl acrylate or methacrylate. Such copolymers can be obtained by polymerization of ethylene in presence of the hydroxyalkylacrylate at high pressure and temperature and using an appropriate peroxide or perester as initiator. The desired polymer viscosity or melt flow rate can be obtained by using known molecular weight modifiers.

The second component (b) of the adhesive composition is a mixture containing trimeric isocyanurate groups and at least two terminally blocked isocyanate groups. It contains at least 10 wt% of isocyanurate derived from an aliphatic or cycloaliphatic diisocyanate, and di-, tri-, tetra-, penta- and possibly hexaisocyanates as a mixture. The isocyanate groups are blocked with an extraneous blocking agent which is released on heating. Preferably the polyisocyanate has no free isocyanate groups and the rate of unblocking and hence crosslinking can be varied by controlling curing temperature.

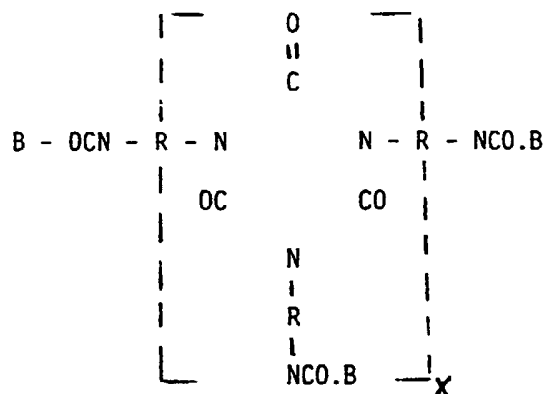
By being blocked or masked, the isocyanate can be protected from reacting with the alcohol functions of the copolymer and reactive groups of the third component until the decomposition temperature of the blocked polyisocyanate is reached. The blocked polyisocyanate may contain other groups than the blocked isocyanates which do not dissociate on heating. Aliphatic or cycloaliphatic polyisocyanates are preferred.

Preferably the blocked polyisocyanate compound is used at a mole ratio OH:NCO of from 4 to 16; especially from 8 to 16 and especially above 10. Good compositions can be obtained using lower amounts of cross-linking agent.

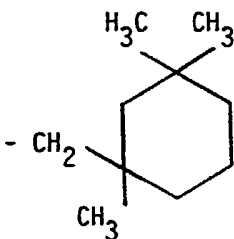
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Isocyanurate derivatives are used advantageously because they can contain more than two blocked isocyanate groups per molecule.

Typical compounds suitable for the invention are :



where X is from 0 to 4, B is a blocking agent and R is



The blocking agent can be lactam, such as ϵ -caprolactam or δ -valerolactams or γ -butyrolactam, preferably ϵ -caprolactam.

These compounds are described in US 4302351.

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A product particularly useful for the invention and believed to have the composition shown above, is marketed by Chemische Werke Huls AG as IPDI B 1530. It is based on 3-isocyanatomethyl-3,3,5-trimethyl-cyclohexylisocyanate also called isophorone diisocyanate and abbreviated as IPDI, it contains approximately 15 wt% of blocked isocyanate. The blocking agent is { -caprolactam.

The adhesive composition may contain a third component, and optionally further components, to decrease the viscosity of the formulation at temperatures below the curing temperature to facilitate handling, to preferably act as an adhesion promoter or to alter the physical properties of the cured compound such as providing a different modulus.

The optional third component of the film or hot melt composition is an hydrocarbon tackifier resin such as the Escorez (Registered Trade Mark) resins commercialised by Exxon Chemical International or synthetic or natural terpene tackifiers. A low molecular weight polyhydroxy compound may optionally also be added.

Suitable polyhydroxy compounds are tri-, or tetra-functional polyether polyols used in the manufacture of polyurethanes. It has been found that a particularly suitable polyether is a 300 gm/mole molecular weight adduct of propylene oxide and glycerol (hydroxyl number 56 mgr KOH/gr). Low molecular weight polypropylene oxide polyols are well known and are commercially available.

In preparing the film or hot melt adhesive composition, the blocked polyisocyanate should be mixed at a temperature below that at which the isocyanate begins to unblock to an appreciable extent. Temperatures from 120 to 130°C have been found adequate when using IPDI B 1530.

When the third component is present typical quantities of the components are 40 to 90 wt %, preferably 50 to 75 weight % of the ethylene copolymer, 10 to 60 weight %, preferably 25 to 50 weight % of the tackifying resin based on the total weight of the two components.

When a low molecular weight polyhydroxy compound is added, typical quantities of the polyhydroxy compound are 1 to 10 weight percent of the total weight of the three components.

The composition containing only the ethylene copolymer and the blocked polyisocyanate can be processed and applied as a film, the composition containing the ethylene copolymer, the blocked polyisocyanate and the tackifying resin and optionally the low molecular weight polyhydroxy compound can be applied as a film or as a hot melt, both at a temperature below which appreciable heat activation of the blocked polyisocyanate takes place, and cured after application by heating to a temperature where the blocked polyisocyanate unblocks sufficiently quickly. When using IPDI B 1530, temperatures in the range 150°C to 200°C are adequate. By using the compositions of this invention and curing them by heating at 150°C to 200°C, it is found that strong adhesive bonds are obtained which are still effective at temperatures as high as 150°C when tested under shear conditions. Good bonding to metal surfaces can be achieved particularly.

Examples

Table 1 sets ethylene copolymers A, B, C, D used for making formulations of the examples, their composition, melting peak temperature as determined by differential scanning calorimetry, melt viscosity (Brookfield viscometer RV, Thermosel), and melt flow rate at 125°C, 325 gm load.

TABLE 1

POLYMERS PROPERTIES

EOVH TYPE	COMPOSITION WEIGHT %			MELTING TEMPERATURE (°C) (1)	MELT VISCOSITY (Pa.s)		MELT FLOW RATE 125°C, 325 gm (gm/10 min.)
	E	VOH	VA		160°C	180°C	
A	82.15	14.75	3.1	99	68.0	36.1	2.17
B	88.7	10.0	1.3	101.5	45.9	25.4	6.4
C	82.3	13.7	4.0	91.0	10.0	5.8	30.4
D	79.8	9.6	10.6	79.4	9.0	5.3	> 30

(1) D.S.C. PEAK ENDOTHERM.

GV1V-94

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The formulations given in Table 2 consist of the ethylene copolymers A, B or C and IPDI B 1530 mixed in a laboratory scale mixer by melting the ethylene copolymer first at 130°C, and introducing the IPDI B 1530 which was mixed for typically 6 minutes.

The mixtures were then pressed to form a 0.1-0.2 mm thick film, which was then applied between 0.09 mm aluminum foils as a substrate. The assembly was placed in a heated press at 180°C for 30 minutes under a pressure of 1-5 kg/cm² so as to produce an adhesive layer of 60 to 130 microns depending on the viscosity of the polymer used. The adhesion T-peel strength, lap shear strength at 100°C and 150°C and Peel Adhesion Failure Temperature (PAFT) were measured and the results are given in Table 3 for the different compositions.

The T-peel strength was determined using a tensometer at a pulling speed of 5.08 cm per minute and a 2 cm wide strip specimen.

The lap shear strength was determined on a 2.54 cm x 2.54 cm bond area, and an adhesive layer about 10 micron thick, using a tensometer at a pulling speed of 5.08 cm per minute. The tensometer was equipped with a heated chamber and the tests were carried out at 100°C and 150°C.

The Peel Adhesion Failure Temperature (PAFT) was carried out using a 2.5 cm wide and 2.5 cm long adhesive bond in the T-peel mode and 0.5 kg load. The temperature was raised continuously at 24°C per hour rate. PAFT is the temperature at which the bond failed.

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Tests carried out on the ethylene copolymer alone, or on the compositions of Table 2 before heating at 180°C for 30 minutes indicated less than 2N/2cm adhesion T-peel strength.

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TABLE 2

CODE AND COMPOSITIONS EVOH - IPDI B 1530
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CODE	EVOH TYPE	MOLE RATIO OH/NCO	COMPOSITION (PARTS)	
			EVOH	IPDI B 1530
A-6	A	6	100	15.63
A-8		8		11.72
A-10		10		9.38
A-12		12		7.82
A-16		16		5.86
<hr/>				
B-4	B	4	100	15.90
B-6		6		10.60
B-8		8		7.95
B-10		8		6.36
B-12		12		5.30
<hr/>				
C-4	C	4	100	21.77
C-6		6		14.52
C-8		8		10.89
C-10		10		8.71
C-12		12		7.26
C-16		16		5.44

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TABLE 3

CODE	T-PEEL STRENGTH (N/2cm)	P.A.F.T. (°C)	LAP SHEAR STRENGTH (N PER SQUARE INCH)	
			AT 100°C	AT 150°C
A-6	20-22	75±3	351	266
A-8	21-22	87±1	358	295
A-10	19-21	92±2	378	300
A-12	18-20	92±1	379	315
A-16	19-21	94±2	363	287
B-4	21-22	72±3	341	247
B-6	21-24	85±1	353	255
B-8	21-23	92±1	356	270
B-10	21-22	93±1	365	274
B-12	15-17	99	360	272
C-4	22-25	55±7	315	240
C-6	23-26	71±2	330	295
C-8	21-25	78±1	340(*)	305
C-10	22-24	83±2	340(*)	315
C-12	21-24	89±1	340(*)	300
C-16	17-23	94±3	350(*)	306

(*) RUPTURE OF AL FOIL SUBSTRATE.

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It is clear from the examples A-6 through A-16, B-4 through B-12, and C-4 through C-16 in Table 3, that high adhesion develops during cure as evidenced by T-peel strength results. High shear strength values at elevated temperature are also obtained after cure. These films can still however be peeled-off at temperatures from 55 to 99°C depending on composition.

Moreover it has been found that the compositions given in Table 2 give after cure rubber-like stress-strain behavior, the cured compositions exhibit high tensile strength, high elongation and high energy at break, significantly higher than the uncured polymer. Table 4 gives the tensile strength, elongation and energy at break after 25 minutes cure at 180°C. The corresponding values for uncured polymer B are 9.29 MPa tensile at break, 60 % elongation at break, and 0.34 Joule energy at break; they are 6.28 MPa, 164 % and 0.56 Joule respectively for polymer C.

The adhesive composition may contain as third component an hydrocarbon tackifier resin. One of the advantages of such a composition is that it can be applied either as a film between two substrates or as a hot melt. An example of hydrocarbon tackifier resin is Escorez^R 1310 from Exxon Chemical. When compounded with EVOH B in a 60 parts polymer - 40 parts Escorez 1310, the melt viscosity at 140°C is 31.3 Pa.s, in a similar composition with EVOH C the melt viscosity at 140°C is 16.0 Pa.s.

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TABLE 4

CODE	TENSILE STRENGTH AT BREAK (MPa)	ELONGATION AT BREAK (%)	ENERGY AT BREAK (J)
A-6	23.4	243	1.40
A-8	24.9	279	1.83
A-10	26.7	319	2.24
A-12	25.1	337	2.34
A-16	23.9	371	2.63
B-4	17.75	204	1.11
B-6	17.8	246	1.49
B-8	22.4	306	2.04
B-10	21.8	317	2.18
B-12	19.4	355	2.4
C-4	16.1	195	0.77
C-6	20.8	260	1.30
C-8	22.9	315	1.72
C-10	22.4	350	1.95
C-12	22.3	383	2.30
C-16	20.0	415	2.28

ASTM D 412 Type D dumbbells, crosshead speed 2 in/min.

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When compositions containing an hydrocarbon tackifier are cured strong adhesive bonds at elevated temperatures are obtained.

The examples given in Table 5 through 8 will illustrate compositions capable of forming such adhesive bonds, as well as the effect of cure temperature and cure time. All these examples were obtained using 90 micron aluminum foil as substrate.

A low molecular weight, polyethylene oxide polyol or polypropylene oxide polyol containing at least three hydroxyl groups per mole may also be added to the compositions. It reduces the viscosity of the hot melt composition and makes the film more tacky whilst maintaining good cured adhesive properties as illustrated by the data given in Table 9. The particular polyether triol used in these samples is an adduct of propylene oxide and glycerol, viscosity at 25°C is 800 mPa.s, hydroxyl number is 56±2.

Using the lactam blocked polyisocyanate isocyanurate derivatives a system is provided which permits low viscosity EVOH polymers to be processed with a crosslinking system in a hot melt formulation with low, if any, viscosity reducing agent. Good processing stability can be achieved at the same time as good ultimate thermal stability and low volatile generation during curing. The selection of a blocking agent which unblocks the isocyanate groups at the appropriate rate is critical and lactams are very desirable for hot melt adhesive purposes.

It is desirable, as the invention permits, to achieve a high crosslinking efficiency and good adhesive and physical properties with a low concentration of blocked polyisocyanate. The blocked polyisocyanate of the type used in this invention can be used at significantly lower concentration than blocked diisocyanates or internally blocked polyisocyanates. The amount of blocking agent released during the cross-linking reaction is also minimized which may be beneficial. It is speculated although not demonstrated that blocked polyisocyanates containing two and more than two isocyanates generate a more efficient crosslinking reaction than diisocyanates.

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TABLE 5

EVOH B BASED HOT MELT PROPERTIES

<u>COMPOSITION (WEIGHT)</u>						
EVOH B	6	→				
ESCOREZ ^R 1310	4	→				
IPDI B 1530	0.477					
(MOLE RATIO OH/NCO)	(8)	→		(10)	→	
CURE TEMPERATURE (°C)	180	→				
CURE TIME (min.)	10	25	60	10	25	60
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LAP SHEAR STRENGTH						
(N/IN ²) AT 100°C	361±44	340±15	321±80	348±70	376±4	359±14
AT 150°C	251±21	272±27	260±5	257±18	262±37	266±25
(FILM THICKNESS, micron)	(20)	(20)	(25)	(20)	(25)	(25)
CURE TEMPERATURE (°C)	200	→		200	→	
CURE TIME (min.)	7	30		7	30	
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LAP SHEAR STRENGTH						
(N/IN ²) AT 100°C	360*±10	331*±28		353*±24	251±25	
150°C	273±19	255±35		320*±26	246±2	
(FILM THICKNESS, micron)	(20)	(15)		(15)	(10)	

(*) RUPTURE OF ALUMINUM FOIL SUBSTRATE

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TABLE 6

EVOH C BASED HOT MELT PROPERTIES

<u>COMPOSITION</u> (WEIGHT)							
EVOH C	6	6	6	6	6	6	6
ESCOREZ ^R 1310	4	4	4	4	4	4	4
IPDI B 1530	-	0.871	0.653	0.522	0.653	0.522	0.436
(MOLE RATIO OH/NCO)	-	(6)	(8)	(10)	(8)	(10)	(12)
CURE TEMPERATURE (°C)	180	—————>			200	—————>	
CURE TIME (MIN.)	25	—————>			7	—————>	
o T-PEEL STRENGTH (N/2cm)	1-2	31-34	32-37	33-35	35-36	28-30	32-35
o P.A.F.T. (°C)	-	77±3	80±4	85±1	79±1	87±1	90±2
o LAP SHEAR STRENGTH (N/IN ²) AT 100°C	0	312±28	367±23	373(a)	360(a)	370(a)	-
AT 150°C	0	226±15	280±20	276±50	276±12	300	-
TENSILE STRENGTH (MPa)	6.7	12.57	11.8	11.4	12.4	11.9	11.7
ELONGATION AT BREAK (%)	16	290	317	330	300	350	370
ENERGY AT BREAK (J)	0.1	1.21	1.24	1.4	1.25	1.6	1.6

(a) RUPTURE OF ALUMINUM FOIL SUBSTRATE

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TABLE 7

EFFECT OF CURE TIME ON PROPERTIES

- o EVOH C 6
 - o ESCOREZ^R 1310 4
 - o IPDI B 1530 0.522
- (MOLE RATIO OH/NCO : 10)

CURE TEMPERATURE (°C)	180	→		
CURE TIME (min.)	5	10	25	120
T-PEEL STRENGTH (N/2cm)	7-15	29-32	33-35	26-30
P.A.F.T. (°C)	84 _{±1}	88 _{±4}	85 _{±1}	86 _{±2}
TENSILE STRENGTH (MPa)	8.0	11.1	11.4	12.5
ELONGATION AT BREAK (%)	380	380	330	360
ENERGY AT BREAK (J)	1.36	1.5	1.4	1.5

TABLE 8

EVOH D BASED HOT MELT PROPERTIES

<u>COMPOSITION</u> (WEIGHT) EVOH D ESCOREZ ^R 1310 IPDI B 1530 (MOLE RATIO OH/NCO)	6 —————→ 4 —————→ 0.916 0.61 0.458 (4) (6) (8)
CURE TEMPERATURE (°C) CURE TIME (min.)	180 —————→ 25 —————→
T-PEEL STRENGTH (N/2cm) P.A.F.T. (°C) LAP SHEAR STRENGTH (N/IN ²) AT 100°C AT 150°C	26-33 29-34 20-24 69±1 81±2 86±4 365(a) 360(a) 278 335(a) 305 180
TENSILE STRENGTH (MPa) ELONGATION AT BREAK (%)	12.2 10.45 8.8 360 420 470
(a) Rupture of aluminum foil substrate.	

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TABLE 9

<u>COMPOSITION</u> (WEIGHT)					
EVOH C	6	—————>		6	—————>
ESCOREZ ^R 1310	3.5	—————>		3	—————>
PPO TRIOL (MW 300)	0.5	—————>		1	—————>
IPDI B 1530	1.10	0.83	0.66	1.34	1.00
(MOLE RATIO SUM OH/NCO)	(6)	(8)	(10)	(6)	(8)
CURE TEMPERATURE (°C)	180	—————>			
CURE TIME (min.)	25	—————>			
T-PEEL STRENGTH (N/2cm)	27-33	24-30	24-28	20-24	17-22
P.A.F.T. (°C)	63±1	76±1	81±2	57±2	73±2
LAP SHEAR STRENGTH					
(N/IN ²) AT 100°C	300	300	300	275	260
AT 150°C	241	231	242	211	223
TENSILE STRENGTH (MPa)	15.1	14.3	13.3	15.5	14.0
ELONGATION AT BREAK (%)	304	355	386	317	366
ENERGY AT BREAK (J)	1.15	1.42	1.47	1.20	1.43

CLAIMS

1. A cross-linkable adhesive composition comprising :
 - (a) a copolymer of at least 50 wt% ethylene and containing from 0.10 to 0.35 mole of hydroxyl functionality per 100 gm of polymer;
 - (b) a compound containing isocyanurate groups and at least two terminally blocked isocyanate groups;
 - (c) optionally a hydrocarbon tackifying resin, and optionally a low molecular weight hydroxy-terminated polyalkylene oxide containing at least three hydroxyl groups or other viscosity reducing agent.
2. A composition according to claim 1 in which the copolymer (a) has a melt viscosity of from 1 to 50 Pa.s at 180°C and the compound (b) is a mixture of blocked polyisocyanates which mixture consists of at least 30 wt% of components containing three and more blocked isocyanate groups.
3. Composition according to Claim 1 or Claim 2, wherein the copolymer has a melt viscosity preferably of from 3 to 40 Pa.s at 180°C.
4. Composition according to any of the preceding claims wherein the blocked polyisocyanate is used at a mole ratio OH:NCO of 4 to 20.

5. Composition according to any of the preceding claims wherein the compound (b) contains blocked cycloaliphatic polyisocyanates.
6. Composition according to any of the preceding claims wherein the polymer is
 - (a) a partially or completely hydrolysed polymer of ethylene derived units and vinyl esters, preferably having from 70 to 93 wt% of ethylene, from 7 to 15 wt% of vinyl alcohol and from 0 to 15 wt% of vinyl acetate; or
 - (b) a polymer containing at least 50 wt% of ethylene and 10 to 45 wt% of 2-hydroxyethyl acrylate or methacrylate.
7. Composition according to any of the preceding claims in which the tackifying resin is non-reactive with isocyanate optionally accompanied by a polyalkylene polyol of average molecular weight from 100 to 2000 containing at least three hydroxyl groups.
8. Composition according to anyone of the preceding claims which comprises 40 to 100 % of the ethylene copolymer, 0 to 60 wt % of the other components, and the blocked polyisocyanate in an amount so as to provide a OH:NCO ratio of from 4 to 20.
9. Composition according to claims 1, 2, 4, 5 and 8 in which the blocking compound is a lactam, such as ϵ -caprolactam.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/EP 91/00577**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 08 G 18/62, 18/79, 18/40, C 09 J 175/04, 123/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 08 G, C 09 J	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁸		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0041192 (SIEMENS) 9 December 1981 see claims 1-5,7; page 4, line 18 - page 5, line 4 cited in the application ---	1
A	EP, A, 0294271 (ATOCHEM) 7 December 1988 see claims 1-7; page 2, line 51 - page 3, line 26 cited in the application -----	1
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
12th June 1991		01.08.91
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		<i>D. Frank</i> Mme Dagmar FRANK

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9100577
SA 45868

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 23/07/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0041192	09-12-81	DE-A- 3021044	24-12-81
		JP-A- 57023422	06-02-82
EP-A- 0294271	07-12-88	FR-A- 2616155	09-12-88
		AU-A- 1743488	08-12-88
		JP-A- 64001781	06-01-89
		US-A- 4908408	13-03-90